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Thermolysis of Half-Sandwich Vanadium(V) Imido Complexes to Generate Vanadium(III) Imido Species via a Vanadium(IV) Intermediate

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Thermolysis of half-sandwich vanadium imido complexes Cp(RN)V(i-Pr_2N)Me (R = p-Tol, **1a**; R = t-Bu, **1b**) results in a mixture of products, including vanadium(IV) dimers $[CpVMe]_2(\mu\text{-RN})_2$, i-$Pr_2$NH, i-PrNC$Me_2$, CH_4, and one or more paramagnetic species. In the presence of dmpe (dmpe = bis(dimethylphosphino)ethane), PMe_3, or PhSSPh, the initially formed paramagnetic species can be trapped, providing Cp(RN)VL_2 (R = p-Tol, L_2 = dmpe, **2a**; R = t-Bu, L_2 = dmpe, **2b**; R = p-Tol, L = PMe_3, **3a**; R = t-Bu, L = PMe_3, **3b**; R = t-Bu, L = SPh, **4b**). This suggests that the initially formed species is [Cp(RN)V]. When generated in situ, [Cp(RN)V] is active in the [2+2+2] cyclotrimerization of PhCCH (R = p-Tol, t-Bu) and PhCCPh (R = t-Bu). Furthermore, the data presented indicate a mechanism in which both $[CpVMe]_2(\mu\text{-RN})_2$ and [Cp(RN)V] originate from a common intermediate, vanadium(IV) imido species [Cp(RN)VMe].

Introduction

Group 4 and 5 imido complexes have gained much interest as hydroamination catalysts.[1] In the case of vanadium, the chemistry of half-sandwich vanadium(V) imido complexes has been extensively studied.[2] By contrast there are only a few examples of imido complexes of vanadium(III). In general these complexes are prepared by reduction of their vanadium(V) dichloride precursors Cp(RN)VCl_2 with magnesium in the presence of phosphine or phosphite ligands or CO.[3] Two notable examples, however, generate half-sandwich vanadium(III) imido complexes via an alternative route. In both cases, vanadium(III) imido complexes are generated by unusual rearrangement reactions involving t-BuCN.[4] Here we report the generation of vanadium(III) imido complexes by thermolysis of Cp(RN)V(i-Pr_2N)Me (R = p-Tol, **1a**; R = t-Bu, **1b**) and their application as catalysts for the [2+2+2] cyclotrimerization of phenylacetylenes.

Results

Compound Cp(p-TolN)V(i-Pr_2N)Me (**1a**)[5] is moderately stable at room temperature, though warming a solution of **1a** in toluene-d_8 to 50 °C results in degradation to a mixture of products. ^{1}H NMR spectroscopy reveals the formation of a mixture of $[CpVMe]_2(\mu\text{-p-TolN})_2$,[6] diisopropylamine, *N*-isopropylisopropylideneamine, methane, and one or more unidentified paramagnetic species (resonances at δ 39.72, 28.55, 19.02, 16.29, 9.32, 5.38, −5.21, and −8.44 ppm). It is interesting to note that the d_0-isotopologue of i-Pr_2NH was observed (see Discussion). We propose that these paramagnetic species are in the V(III) oxidation state and are EPR silent at RT and 77 K.[7] On the basis of the stoichiometry of the reaction, we tentatively identify this species as [Cp(p-TolN)V] or at least to a compound of this general formula. However, attempts to convert such species into low-spin vanadium(III) dmpe adducts (dmpe = bis(dimethylphosphino)ethane) did not provide the corresponding complex

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(1) For reviews on catalytic hydroamination reactions, see: (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (b) Nobis, M.; Driessen-Hölscher, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983. (c) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (d) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935. (e) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (f) Doye, S. *Synlett* **2004**, 1653. (g) Odom, A. L. J. *Chem. Soc., Dalton Trans.* **2005**, 225.

(2) (a) Preuss, F.; Fuchslocher, E.; Sheldrick, W. S. *Z. Naturforsch.* **1985**, *40b*, 1040. (b) Preuss, F.; Noichl, H.; Kaub, J. *Z. Naturforsch.* **1986**, *41b*, 1085. (c) Preuss, F.; Becker, H. *Z. Naturforsch.* **1986**, *41b*, 185. (d) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408. (e) Preuss, F.; Becker, H.; Hausler, H.-J. *Z. Naturforsch.* **1987**, *42b*, 881. (f) Preuss, F.; Becker, H.; Kaub, J.; Sheldrick, W. S. *Z. Naturforsch.* **1988**, *43b*, 1195. (g) Preuss, F.; Fuchslocher, E.; Leber, E.; Towae, W. *Z. Naturforsch.* **1989**, *44b*, 271. (h) Preuss, F.; Becker, H.; Wieland, T. *Z. Naturforsch.* **1990**, *45b*, 191. (i) De With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1990**, *9*, 2207. (j) Preuss, F.; Wieland, T.; Gunther, B. *Z. Anorg. Allg. Chem.* **1992**, *609*, 45. (k) Preuss, F.; Overhoff, G.; Becker, H.; Hausler, H.-J.; Frank, W. *Z. Anorg. All. Chem.* **1993**, *619*, 1827. (l) De With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903. (m) De With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493.

(3) (a) Buijink, J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922. (b) Preuss, F.; Billen, M.; Tabellion, F.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2446. (c) Billen, M.; Hornung, G.; Preuss, F. *Z. Naturforsch.* **2003**, *58b*, 975.

(4) (a) Hessen, B.; Buijink, J. K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2268. (b) Buijink, J.-K. F.; Kloetstra, K. R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1996**, *15*, 2523.

(5) Bouwkamp, M. W.; Batinas, A. A.; Witte, P. T.; Hubregtse, T.; Dam, J.; Meetsma, A.; Teuben, J. H.; Hessen, B. *Organometallics* **2008**, *27*, 4071.

(6) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *J. Organomet. Chem.* **1995**, *497*, 161.

(7) (a) Alonso, P. J.; Forniés, J.; García-Monforte, M. A.; Martín, A.; Menjón, B. *Chem. Commun.* **2001**, 2138. (b) Krzystek, J.; Fiedler, A. T.; Sokol, J. J.; Ozarowski, A.; Zvyagin, S. A.; Brunold, T. C.; Long, J. R.; Brunel, L. C.; Telser, J. *Inorg. Chem.* **2004**, *43*, 5645.

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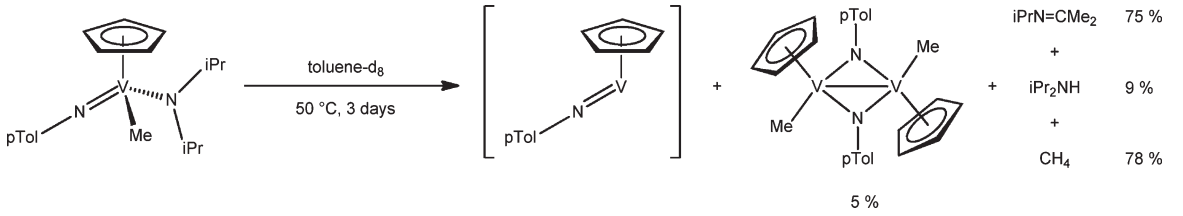
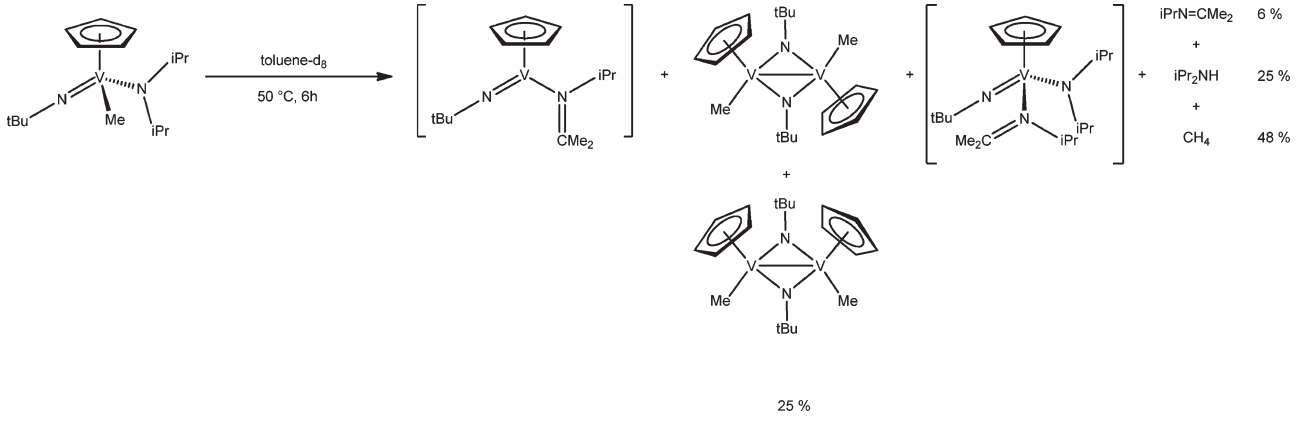
Scheme 1



Scheme 2



Cp(p-TolN)V(dmpe) (vide infra). See Scheme 1 for an overview of the constituents of the reaction mixture, including their relative amounts.[8]

Compound Cp(t-BuN)V(i-Pr_2N)Me (**1b**), which was prepared by addition of MeLi to the corresponding chloride precursor Cp(t-BuN)V(i-Pr_2N)Cl,[9] also decomposes to generate a mixture of products. In this case thermolysis at 50 °C is complete within 6 h by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum includes contributions from two diamagnetic species, and a mixture of presumably more than one paramagnetic species was observed (δ 91.45, 58.88, 38.30, 17.55, 15.40, 12.07, 10.06, 5.02, and −6.44 ppm), as well as i-Pr_2NH, i-PrNCMe_2, and methane (Scheme 2).[8] The diamagnetic species were tentatively assigned as the cis- and trans-isomers of the vanadium dimer [CpVMe]$_2$(μ-t-BuN)$_2$. Vroegop et al. previously reported the synthesis of the corresponding titanium compound [CpTiCl]$_2$(μ-t-BuN)$_2$.[10] This compound was initially obtained as the kinetic trans-isomer, which undergoes thermal equilibration (4:1) in favor of the cis-isomer.

Addition of the oxidant $PbCl_2$ to the reaction mixture results in the formation of Cp(t-BuN)V(i-Pr_2N)Cl[9] and an additional amount (20%) of *N*-isopropylisopropylideneamine, indicating that one of the paramagnetic species is the vanadium(IV) compound Cp(t-BuN)V(i-Pr_2N)(i-PrNCMe_2). This compound could be identified by EPR spectroscopy, which shows, prior to oxidation, a signal corresponding to a d_1-vanadium compound with a typical octet hyperfine structure with $a(^{51}V)$ = 18 G. Although this coupling is small compared to most other vanadium(IV) sandwich and half-sandwich complexes known in the literature (61−80 G),[11] it is larger than the hyperfine coupling found in complexes of the type Cp*$_2$VNAr (Ar = aryl; 5−10 G).[12]

In the case of the decomposition of **1b**, addition of dmpe to the initially obtained reaction mixture did result in the formation of the dmpe adduct of the expected vanadium(III) imido species, Cp(t-BuN)V(dmpe) (**2b**, see below). Apart from the spectral features for compound **2b**, the ^{1}H NMR spectrum of the reaction mixture revealed that one of the paramagnetic species had disappeared (the remaining paramagnetic species shows resonances at δ 15.40, 12.11, 10.06, and −6.44 ppm). In addition, an additional amount (22%) of *N*-isopropylisopropylideneamine was observed, indicating that the vanadium(III) imido species was initially supported by an imine ligand.

When the thermolysis of **1a** and **1b** was carried out in the presence of a small excess (1.2 equiv) of dmpe, the corresponding dmpe adducts, Cp(RN)V(dmpe) (R = p-Tol: **2a**; R = t-Bu: **2b**, Scheme 3), were trapped. ^{1}H NMR spectroscopy revealed that in both cases this is the major species observed (90% and 94% conversion, respectively). In the case of compound **2a**, a small amount of the vanadium dimer [CpVMe]$_2$(μ-p-TolN)$_2$ was observed also (6%), whereas the only other half-sandwich vanadium species observed in the case where **2b** is the starting material. The formation of the expected amounts of i-Pr_2NH, i-PrNCMe_2, and methane were observed in both reactions.

(8) The amount of [CpVMe]$_2$(μ-p-TolN)$_2$, diisopropylamine, and *N*-isopropylisopropylideneamine was determined using integration of representative signals in the ^{1}H NMR spectrum of the reaction mixture; the amount of methane was quantified using a Toepler pump.

(9) Preuss, F.; Steidel, M.; Vogel, M.; Overhoff, G.; Hornung, G.; Towae, W.; Frank, W.; Rein, G.; Muller-Becker, S. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1220.

(10) (a) Vroegop, C. T.; Teuben, J. H.; Van Bolhuis, F.; Van der Linden, J. G. M. *J. Chem. Soc., Chem. Commun.* **1983**, 550. (b) Jekel-Vroegop, C. T.; Teuben, J. H. *J. Organomet. Chem.* **1985**, *286*, 309.

(11) (a) Foust, D.-F.; Rausch, M. D.; Samuel, E. *J. Organomet. Chem.* **1980**, *193*, 209. (b) Mishra, S. P.; Singh, S. *J. Mol. Struct.* **1984**, *112*, 59. (c) Nieman, J.; Teuben, J. H. *Organometallics* **1986**, *5*, 1149. (d) Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P. *Organometallics* **1995**, *14*, 4471. (e) Ghosh, P.; Kotchevar, A. T.; DuMez, D. D.; Ghosh, S.; Peiterson, J.; Uckun, F. M. *Inorg. Chem.* **1999**, *38*, 3730. (f) Honzıcek, J.; Palackova, H.; Cisarova, I.; Vinklarek, J. *J. Organomet. Chem.* **2006**, *691*, 202.

(12) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945.

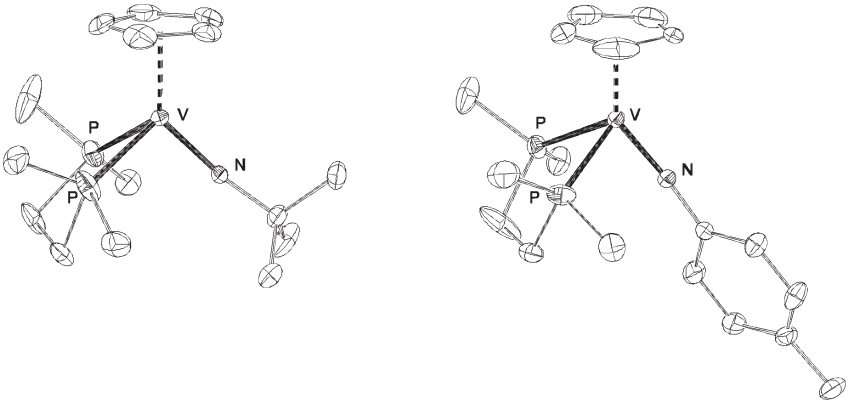
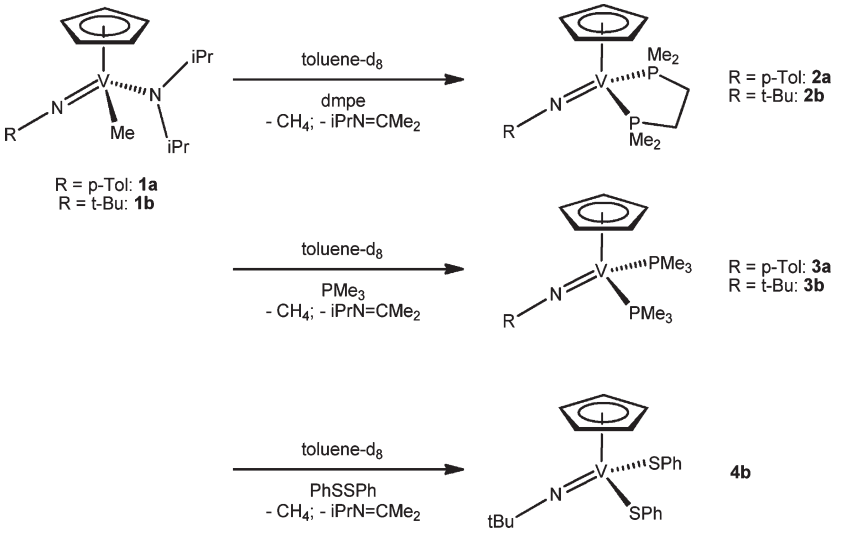


Figure 1. ORTEP representations at the 50% probability level of **2a** and **2b**.

Scheme 3



Compounds **2a** and **2b** were prepared on a preparative scale by warming toluene solutions of **1a** and **1b** in the presence of 1 equiv of dmpe. The compounds were isolated in 55% and 45% yield, respectively, as purple and green crystals. Both compounds were studied using single-crystal X-ray diffraction (see Figure 1 for an ORTEP representation and Table 1 for selected bond distances and angles). The structures of **2a** and **2b** are very similar. Both compounds adopt a three-legged piano-stool geometry. The V−N bond distances (1.7193(18) and 1.6903(1) Å, respectively) are characteristic for a V−N double bond and are similar to those reported elsewhere.[2e,f,j,3a,4,5,13] Furthermore, the V−N−C bond angle is, as expected, close to linear (172.13(16)° and 172.15(16)°). The compounds were further identified by a typical "horned" plateau in the ^{31}P NMR spectrum (**2a**: δ 87.41 ppm, $\Delta\nu_{top} = 2485$ Hz; **2b**: δ 87.34 ppm, $\Delta\nu_{top} = 2696$ Hz)[14] and a single resonance in the ^{51}V NMR spectrum (**2a**: δ −4.9 ppm, $J_{VP} = 341$ Hz; **2b**: δ −381 ppm, $\Delta\nu_{1/2} = 5190$ Hz).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds 2a and 2b

	2a	2b
V−N	1.7193(18)	1.6903(1)
V−P1	2.3596(7)	2.3507(7)
V−P2	2.3522(7)	2.3522(7)
Cp[a]−V	2.275	2.277(9)
N−C	1.380(3)	1.451(3)
V−N−C	172.13(16)	172.15(16)
P1−V−P2	80.95(2)	80.95(2)
P1−V−N	94.42(6)	96.56(6)
P2−V−N	88.41(6)	96.26(6)

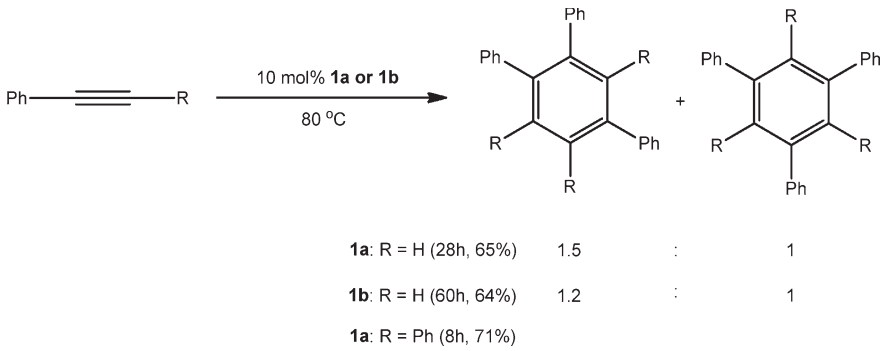
[a] Cp is defined as the centroid defined by the five carbon atoms of the cyclopentadienyl ligands.

The vanadium(III) imido species [Cp(RN)V] was also trapped with PMe_3 or PhSSPh (Scheme 3). Thermolysis of **1a** and **1b** in the presence of PMe_3 (2 equiv) affords the corresponding bis-trimethylphosphine adducts Cp(RN)V-$(PMe_3)_2$ (R = p-Tol: **3a**; R = t-Bu: **3b**) in a 82% and 86% yield (determined by integration of the ^{1}H NMR spectrum of the reaction mixture using Cp_2Fe as internal standard). In addition to the formation of compound **3a**, a small amount of dimer $[CpVMe]_2(\mu$-p-TolN$)_2$ was observed (5%) as well as the same paramagnetic species that was observed after thermolysis in the absence of any of the other trapping agent.

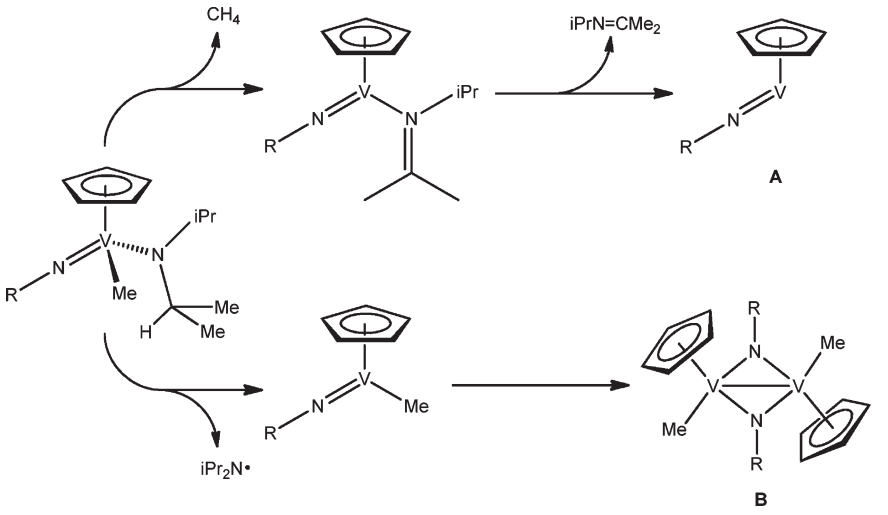
(13) (a) Preuss, F.; Wieland, T.; Perner, J.; Heckmann, G. *Z. Naturforsch.* **1992**, *47b*, 1355. (b) Witte, P. T.; Meetsma, A.; Hessen, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1997**, *119*, 10561. (c) Preuss, F.; Perner, J.; Frank, W. A.; Reiss, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 901. (d) Billen, M.; Hornung, G.; Wolmershauser, G.; Preuss, F. *Z. Naturforsch.* **2003**, *58b*, 237. (e) Sato, Y.; Nakayama, Y.; Yasuda, H. *J. Appl. Polym. Sci.* **2005**, *97*, 1008.

(14) Billen, M.; Hornung, G.; Preuss, F. *Z. Naturforsch.* **2003**, *58b*, 975.

Scheme 4



Scheme 5



This indicates that PMe_3 is less efficient in trapping a species of the type [Cp(RN)V], relative to the chelating dmpe. Cp(t-BuN)V(PMe_3)$_2$ was prepared previously by Preuss and coworkers by reduction of the corresponding dichloride precursor Cp(t-BuN)VCl_2 with Mg in the presence of 2 equiv of PMe_3.[14,15] For compounds **3a** and **3b** resonances at 54.45 and 52.3 ppm are observed by ^{31}P NMR spectroscopy and triplets at δ 267.59 (J_{VP} = 399.66 Hz) and −111.39 (J_{VP} = 420.58 Hz) ppm by ^{51}V NMR spectroscopy. In the case of the thermolysis of **1b** in the presence of PhSSPh, the formation of vanadium(V) bisthiolate species Cp(t-BuN)V(SPh)$_2$ (**4b**) was observed,[13d] the result of an oxidative addition of the disulfide reagent to the d^2-vanadium center (Scheme 3).

The propensity of the [Cp(RN)V] species to undergo oxidative addition reactions was utilized in the catalytic [2+2+2] cyclotrimerization of phenylacetylenes PhCCR (R = H, Ph). Heating a PhCCH solution in benzene-d_6 in the presence of 10 mol % of compounds **1a** or **1b** to 80 °C for 28 and 8 h, respectively, resulted in 88% and 90% conversion of the alkyne to form a mixture of products. The main product observed is 1,2,4- and 1,3,5-triphenylbenzene (**1a**: 65% yield, 1.5:1 ratio; **1b**: 64% yield, 1.2:1 ratio), with small amounts of dimers, tetramers, and higher oligomers observed as well. In the case of compound **1a**, the trimerization of diphenylacetylene resulted in 80% conversion of the substrate to yield 71% of hexaphenylbenzene (Scheme 4).

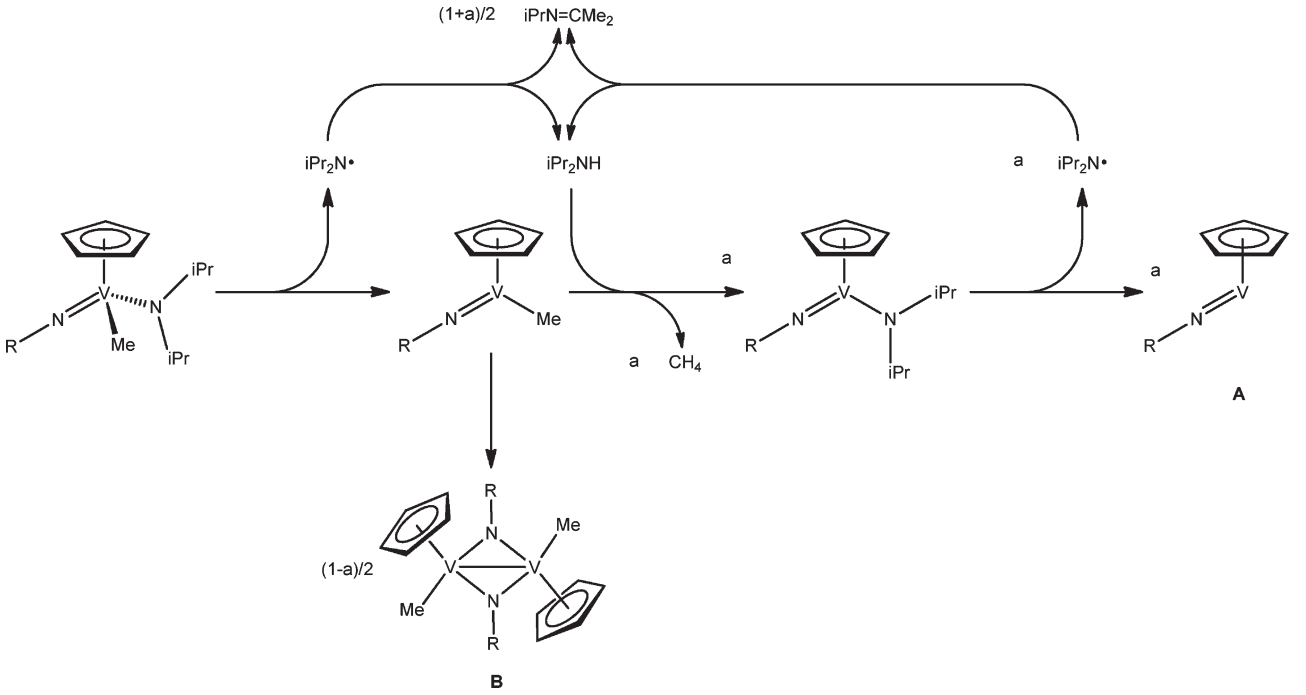
(15) Preuss, F.; Billen, M.; Tabellion, F.; Wolmershauser, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2446.

Discussion

In the present study the trapping of vanadium imido species using a series of trapping agents was examined. The main finding is that the yield of the vanadium(III) imido species increased significantly when dmpe was employed as trapping agent. The more conventional route to species **A** and **B** is depicted in Scheme 5. Compound **A** is generated by β-hydrogen transfer involving one of the i-Pr methine protons and the methyl ligand to generate *N*-isopropylisopropylideneamine and methane, whereas species **B** is the result of a homolysis of the V−N bond of the diisopropylamide ligand, followed by dimerization of the resulting vanadium(IV) species, [Cp(RN)VMe]. The mechanism shown in Scheme 5, however, does not rationalize (i) the increased yield of the vanadium(III) imido species **A** upon addition of dmpe and (ii) that the generation of diisopropylamine during this reaction is observed as its d_0-isotopologue. In the case of the mechanism described in Scheme 5, the d_1-isotopologue is expected where the hydrogen atom source is the solvent.

Therefore, an alternative mechanism can be proposed, in which the formation of both species **A** and **B** and the effect of the dmpe ligand and the absence of deuterium incorporation in the diisopropylamine generated are rationalized. The mechanism is depicted in Scheme 6 and involves initial homolysis of the vanadium−nitrogen bond of the diisopropylamide ligand to generate a vanadium(IV) species [Cp(RN)VMe] and the diisopropylamide radical. The latter disproportionates to generate equimolar amounts of diisopropylamine and

Scheme 6



N-isopropylisopropylideneamine.[16] The initially generated vanadium(IV) species [Cp(RN)VMe] can either dimerize to generate the vanadium dimer $[CpVMe]_2(\mu\text{-}RN)_2$ or alternatively react with diisopropylamine to generate the vanadium(IV) amide species, Cp(RN)V(i-Pr_2N). The latter can undergo a second homolysis reaction to generate vanadium(III) species [Cp(RN)V] and an additional equivalent of the diisopropylamide radical. In the presence of dmpe, the formation of the vanadium dimer $[CpVMe]_2(\mu\text{-}RN)_2$ is surpressed, increasing the yield of dmpe adducts **2a** and **2b**. In addition, the hydrogen atom source for the formation of diisopropylamine is another equivalent of the diisopropylamide radical, which would anticipate only the formation of the d_0-isotopologue of i-Pr_2NH, as is observed. Finally, the formation of the vanadium(IV) species Cp(t-BuN)V(i-Pr_2N)(i-PrNCMe_2) further supports the intermediacy of Cp(NR)V(N-i-Pr_2) in the thermolysis reaction.

Conclusions

A new route to half-sandwich vanadium(III) imido species is reported. As a side-product, the vanadium dimer $[CpVMe]_2(\mu\text{-}RN)_2$ is observed also. The observation of i-Pr_2NH rather than i-Pr_2ND in the reaction mixture, as well as the increased yield of the vanadium(III) imido species upon addition of dmpe, suggests a mechanism in which both products originate from the same intermediate. This intermediate is a vanadium(IV) imido species [Cp(RN)VMe], the result of a homolysis of the vanadium−amido bond. The in situ-generated vanadium(III) imido species can be trapped using phosphine ligands and PhSSPh or used as a [2+2+2] cyclotrimerization catalysts for phenylacetylenes to generate substituted benzenes.

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk line, vacuum line, and glovebox techniques. Reagents were obtained from commercial suppliers and used as received unless stated otherwise. Solvents were passed, under a dinitrogen atmosphere, over a column containing BASF R3-11 supported Cu-based scavenger and a mixture of alumina and either 3 Å mol sieves (toluene) or 4 Å mol sieves (pentane, toluene, Et_2O) before use. Benzene-d_6 was dried on Na/K alloy and transferred in vacuo prior use. PhCCH was dried over CaH_2, and Cp(p-TolN)V(N-i-Pr_2)Me was prepared according to the literature procedures.[5] NMR spectra were recorded on Varian VXR-300 (300 MHz), Varian Mercury Plus (400 MHz), or Unity (500 MHz) spectrometers. Chemical shifts were determined relative to the residual solvent peaks and referenced to TMS. ^{51}V NMR chemical shifts are reported in ppm relative to $VOCl_3$, which is used as an external reference ($VOCl_3$, $\delta = 0$ ppm). EPR spectra (X-band, 9.46 GHz) were recorded on a Bruker ECS106 instrument. GC analyses were performed on a HP 6890 instrument with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC-MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany).

Thermolysis of Cp(N-p-Tol)V(i-Pr_2N)Me. In an NMR tube equipped with a Teflon (Young) valve, Cp(p-TolN)V(i-Pr_2N)Me (0.055 g, 0.16 mmol) was dissolved in benzene-d_6 (0.6 mL). The tube was attached to the vacuum line and degassed using three freeze−pump−thaw cycles, after which the tube was placed in an oven at 50 °C for 3 days. The tube was attached to the vacuum line, and the amount of methane formed in the reaction was determined using a Toepler pump (0.78 equiv of CH_4). The volatiles were transferred to a second tube and analyzed by ^{1}H NMR spectroscopy using Cp_2Fe as internal standard and GC-MS analysis. This revealed formation of diisopropylamine ($m/z = 101$) and *N*-isopropylisopropylideneamine ($m/z = 99$) in 9% and 75% yield, respectively. i-Pr_2NH: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 2.79 (sept, J_{HH} = 6.2 Hz, 2H C*H*Me_2), 0.96 (d, J_{HH} = 6.2 Hz, 12H, CH*Me*$_2$), 0.23 (br, 1H NH) ppm. i-PrNCMe_2: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 3.44 (sept, J_{HH} = 6.2 Hz, 1H C*H*Me_2), 1.80 (s, 3H, CMe_2), 1.36 (s, 3H CMe_2), 1.15 (d, J_{HH} = 6.2 Hz, 6H, CH*Me*$_2$)

(16) (a) Seetula, J.; Kalliorinne, K.; Koskikallio, J. *J. Photochem. Photobiol.* **1998**, *43A*, 31. (b) Janovsky, I.; Knolle, W.; Naumov, S.; Williams, F. *Chem.—Eur. J.* **2004**, *10*, 5524.

ppm. The residue was redissolved in benzene-d_6. ^{1}H NMR analysis revealed the presence of both diamagnetic and paramagnetic species. For the paramagnetic species: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 39.7 (br, $\Delta\nu_{1/2}$ = 403 Hz), 28.6 (br, $\Delta\nu_{1/2}$ = 340 Hz), 19.0 (br, $\Delta\nu_{1/2}$ = 276 Hz), 16.3 (br, $\Delta\nu_{1/2}$ = 177 Hz), 9.3 (br, $\Delta\nu_{1/2}$ = 193 Hz), 5.4 (br, $\Delta\nu_{1/2}$ = 33 Hz), −5.2 (br, $\Delta\nu_{1/2}$ = 25 Hz), −8.4 (br, $\Delta\nu_{1/2}$ = 52 Hz) ppm. The diamagnetic species was identified as [CpVMe]$_2$(μ-p-TolN)$_2$. EPR (benzene-d_6, 298 K): g = 1.97; a(^{51}V) = 18 G.

[CpVMe]$_2$(μ-p-TolN)$_2$. A solution of Cp(N-p-Tol)V(i-Pr$_2$N)-Me (0.40 g, 1.2 mmol) in toluene (3 mL) was warmed at 50 °C for 3 days. Slow cooling to room temperature afforded red-brown crystals, which were separated. The compound was identified by ^{1}H NMR spectroscopy as [CpVMe]$_2$(μ-p-TolN)$_2$ and were obtained in 30% isolated yield.

Cp(t-BuN)V(i-Pr$_2$N)Me. To a cold (−40 °C) solution of Cp(t-BuN)V(i-Pr$_2$N)Cl (7.16 g, 22.2 mmol) in diethyl ether (150 mL) was added dropwise MeLi (14 mL, 1.6M, 22 mmol). The mixture was warmed to −10 °C and stirred for 1 h. The color of the solution changed from red to yellow-brown. The workup was carried out at −10 °C. After removal of the solvent in vacuo, the residual ether was stripped off by addition of 2 × 20 mL of cold pentane and subsequent removal of the volatiles in vacuo. Extraction of the reaction mixture with cold pentane (100 mL) and removal of the solvent in vacuo at −10 °C yielded 5.65 g (18.7 mmol, 84%) of the title compound as a brown oil, which crystallizes at −30 °C. ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 5.66 (s, 5H, Cp), 4.40 (sept, J_{HH} = 6.5 Hz, 1H, i-Pr CH), 3.19 (m, 1H, i-Pr CH), 1.65 (d, J_{HH} = 6.4 Hz, 3H, i-Pr Me), 1.24 (s, 9H, t-Bu Me), 1.33 (d, J_{HH} = 6.5 Hz, 3H, i-Pr Me), 0.90 (d, J_{HH} = 6.5 Hz, 3H, i-Pr Me), 0.83 (d, J_{HH} = 6.6 Hz, 3H, i-Pr Me), 0.41 (br, 3H, V-Me) ppm. ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 104.93 (Cp), 62.03 (i-Pr CH), 52.90 (i-Pr CH), 32.36 (i-Pr Me), 31.76 (t-Bu Me), 27.09 (i-Pr Me), 20.41 (i-Pr Me), 19.38 (i-Pr Me), Cq of t-Bu and V-Me not observed. ^{51}V NMR (131 MHz, benzene-d_6, 25 °C, $VOCl_3$ external standard): δ −667.98 (t, J_{VN} = 86.60 Hz).

Thermolysis of Cp(t-BuN)V(i-Pr$_2$N)Me. In an NMR tube equipped with a Teflon (Young) valve, Cp(t-BuN)V(i-Pr$_2$N)Me (0.050 g, 0.17 mmol) was dissolved in benzene-d_6 (0.6 mL). The tube was attached to the vacuum line and degassed using three freeze−pump−thaw cycles, after which the tube was placed in an oven at 50 °C for 6 h. The tube was attached to the vacuum line, and the amount of methane formed in the reaction was determined using a Toepler pump (0.48 equiv of CH_4). The volatiles were transferred to a second tube and analyzed by ^{1}H NMR spectroscopy using Cp_2Fe as internal standard and GC-MS analysis. This revealed formation of diisopropylamine and *N*-isopropylisopropylideneamine in 25% and 6% yield, respectively. The residue was redissolved in benzene-d_6. ^{1}H NMR analysis revealed the presence of both diamagnetic and paramagnetic species. For the paramagnetic species: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 91.5 (br, $\Delta\nu_{1/2}$ = 336 Hz), 58.9 (br, $\Delta\nu_{1/2}$ = 257 Hz), 38.3 (br, $\Delta\nu_{1/2}$ = 96 Hz), 17.6 (br, $\Delta\nu_{1/2}$ = 234 Hz), 15.4 (br, $\Delta\nu_{1/2}$ = 390 Hz), 12.1 (br, $\Delta\nu_{1/2}$ = 156 Hz), 10.1 (br, $\Delta\nu_{1/2}$ = 208 Hz), 5.0 (br, $\Delta\nu_{1/2}$ = 345 Hz), −6.4 (br, $\Delta\nu_{1/2}$ = 1375 Hz) ppm. For the diamagnetic species two major resonances at δ 6.30 and 5.27 ppm are observed in a 1:4 ratio.

Generation of Cp(p-TolN)V(dmpe). In an NMR tube equipped with a Teflon (Young) valve, Cp(p-TolN)V(i-Pr$_2$N)Me (0.058 g, 0.172 mmol) and Cp_2Fe (0.032 g, 0.172 mmol, internal standard) were dissolved in benzene-d_6 (0.6 mL). To the resulting solution was added dmpe (0.026 g, 0.172 mmol). The tube was attached to the vacuum line and degassed using three freeze−pump−thaw cycles, after which the tube was placed in the oven at 50 °C for 3 days. Subsequently the tube was attached to the vacuum line, and the amount of methane formed during the reaction was measured using a Toepler pump (0.84 equiv of CH_4). ^{1}H NMR analysis confirmed the presence of *N*-isopropylisopropylideneamine (88%), diisopropylamine (6%), the title compound (88%), and [CpVMe]$_2$(μ-p-TolN)$_2$ (6%). Spectral data for Cp(p-TolN)V-(dmpe): ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 7.06 (d, J_{HH} = 8.0 Hz, 2H, p-TolN), 6.90 (d, J_{HH} = 8.0 Hz, 2H, p-TolN), 4.99 (br, 5H, Cp), 2.13 (s, 3H, pTolN Me), 1.71−1.49 (m, 2H, PCH_2), 1.43−1.32 (m, 6H, PMe_2), 1.17−0.97 (m, 2H, PCH_2), 0.67−0.45 (m, 6H, PMe_2). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 128.96 (p-TolN CH), 125.34 (p-TolN CH), 92.58 (Cp CH), 32.16 (PCH_2), 21.15 (p-TolN Me), 17.51 (PMe_2). Cq of p-TolN not observed. ^{31}P{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 87.51 (plateau, $\Delta\nu_{top}$ = 2449 Hz). ^{51}V NMR (131 MHz, benzene-d_6, 25 °C, $VOCl_3$ external standard): δ −4.90 (t, J_{PV} = 340.9 Hz).

Cp(p-TolN)V(dmpe). One equivalent of dmpe (0.12 g, 0.80 mmol) was added to a solution of Cp(p-TolN)V(i-Pr$_2$N)Me (0.27 g, 0.80 mmol) in toluene (20 mL). The reaction mixture was warmed to 50 °C and stirred for 48 h. The solvent was removed in vacuo, and the mixture was stripped twice with pentane (5 mL). The solvent was removed in vacuo, and pentane (2 × 5 mL) was added and pumped off, to remove residual toluene. Upon concentrating the solution to 10 mL and cooling to −80 °C, 0.16 g (0.44 mmol, 55%) of reddish-purple block crystals of the title compound were obtained. Anal. Calcd for $C_{18}H_{28}NP_2V$: C, 59.07; H, 8.09; N, 3.63. Found: C, 58.7; H, 7.69; N, 3.82.

Generation of Cp(t-BuN)V(dmpe). In an NMR tube equipped with a Teflon (Young) valve, Cp(t-BuN)V(i-Pr$_2$N)Me (0.060 g, 0.20 mmol) was dissolved in benzene-d_6 (0.6 mL). To the resulting solution was added dmpe (0.030 g, 0.20 mmol). The tube was attached to the vacuum line and degassed using three freeze−pump−thaw cycles, after which the tube was placed in the oven at 50 °C for 6 h. Subsequently the tube was attached to the vacuum line and the amount of methane formed during the reaction was measured using a Toepler pump (0.94 equiv of CH_4). ^{1}H NMR analysis confirmed the presence of *N*-isopropylisopropylideneamine and the title compound (94%). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 4.87 (s, 5H Cp), 1.41−1.28 (m, 8H, overlapping resonances for PMe_2 and PCH_2), 1.27 (s, 9H, t-BuN), 1.10 (m, 2H, PCH_2), 0.68 (m, 6H, PMe_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 89.88 (Cp CH), 34.60 (t-BuN Me), 32.44 (PCH_2), 24.55 (PMe_2), 17.92 (PMe_2), Cq of t-Bu not observed. ^{31}P{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 87.34 (plateau, $\Delta\nu_{top}$ = 2689 Hz). ^{51}V NMR (131 MHz, benzene-d_6, 25 °C, $VOCl_3$ external standard): δ −381 ($\Delta\nu_{1/2}$ = 5190 Hz).

Cp(t-BuN)V(dmpe). Dmpe (0.116 g, 0.771 mmol) was added at ambient temperature to a solution of Cp(t-BuN)V(i-Pr$_2$N)Me (0.233 g, 0.771 mmol) in toluene (20 mL). The red-brown solution was warmed to 50 °C and stirred overnight. The solvent was removed in vacuo, and pentane (2 × 5 mL) was added and pumped off, to remove residual toluene. The residue was extracted with 20 mL of pentane. The solution was concentrated to 10 mL and cooled to −80 °C, affording 0.10 g (0.30 mmol, 45%) of green block-shaped crystals of the title compound. Anal. Calcd for $C_{15}H_{30}NP_2V$: C, 54.54; H, 9.44; N, 3.98. Found: C, 54.10; H, 9.12; N, 4.21.

X-ray Analysis of Cp(RN)V(dmpe) (R = p-Tol, t-Bu). Suitable crystals of **3.1**, **3.5**, and **3.6** were mounted on top of a glass fiber in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream on a Bruker SMART APEX CCD diffractometer. Intensity data were corrected for Lorentz and polarization effects, scale variation, and decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS). The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, whose coordinates and isotropic displacement parameters were refined. All refinement and geometry calculations were performed with the

Table 2. Crystallographic Data for 2a and 2b

	2a	2b
formula	$C_{18}H_{28}NP_2V$	$C_{15}H_{30}NP_2V$
fw	371.32	337.30
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
temperature (K)	100(1)	100(1)
a (Å)	10.404(1)	15.1320(1)
b (Å)	10.939(1)	8.9402(6)
c (Å)	17.404(2)	13.7110(1)
β (deg)	95.317(2)	102.480(1)
V (Å^3)	1972.2(3)	1811.0(2)
Z	4	4
ρ_{calc} (g cm^{-3})	1.250	1.237
$F(000)$	784	720
μ(Mo Kα) (cm^{-1})	6.62	7.14
θ range (deg)	2.71−29.25	2.74−26.73
$R(F)$	0.0470	0.0399
$wR(F^2)$	0.1092	0.0950
GooF	1.042	1.021
obsd reflns for $F_0 \geq 4.0\sigma(F_0)$	3837	3028
params	317	294

program packages SHELXL and PLATON. Crystal data and details on data collection and refinement are presented in Table 2.

Generation of CpV(N-*p*-tolyl)(PMe_3)$_2$. In an NMR tube equipped with a Teflon (Young) valve, Cp(p-TolN)V(i-Pr_2N)Me (0.03 g, 0.08 mmol) and Cp_2Fe (0.015 g, 0.08 mmol) were dissolved in benzene-d_6 (0.5 mL). To the resulting solution was added PMe_3 (0.01 g, 0.02 mL, 0.16 mmol). This solution was warmed to 50 °C for 48 h. After this time the color of the mixture had changed from red-brown to brown-green. The spectroscopic data confirmed the formation of CpV(N-*p*-tolyl)-(PMe_3)$_2$ in 82% yield (relative to Cp_2Fe internal standard). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 7.14 (d, J_{HH} = 8.1 Hz, 2H, p-TolN CH), 6.94 (d, J_{HH} = 7.7 Hz, 2H, p-TolN CH), 4.88 (s, 5H, Cp), 2.16 (s, 3H, p-TolN Me), 1.03 (m, 18H, PMe_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 161.52 (p-TolN C_{ipso}), 129.06 (p-TolN CH), 128.72 (p-TolN C_{ipso}), 125.56 (p-TolN CH), 94.49 (Cp), 23.29 (dd, J_{CP} = 10.3, 5.9 Hz, PMe_3), 21.22 (p-TolN Me). ^{31}P{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 54.45. ^{51}V NMR (131 MHz, benzene-d_6, 25 °C, $VOCl_3$ external standard): δ 267.59 (t, J_{VP} = 399.66 Hz).

Generation of CpV(N-*t*-Bu)(PMe_3)$_2$. In an NMR tube equipped with a Teflon (Young) valve, Cp(t-BuN)V(i-Pr_2N)Me (0.040 g, 0.13 mmol) was dissolved in benzene-d_6. To the solution PMe_3 (0.020 g, 0.26 mmol) was added. The tube was warmed at 50 °C for 6 h, and the color changed to green-brown. The volatiles were removed in vacuo, affording the title compound as a brown-green oil (86% yield, Cp_2Fe internal standard). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 4.81 (s, 5H, Cp), 1.07 (s, 9H, t-BuN Me), 0.82 (s, 18H, PMe_3). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 92.00 (Cp), 67.8 (t-BuN Cq), 34.54 (t-BuN Me), 25.02 (dd, J_{CP} = 9.6, 4.8 Hz, PMe_3). ^{31}P{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 52.30 (plateau, $\Delta\nu_{top}$ = 2914.98 Hz). ^{51}V NMR (131 MHz, benzene-d_6, 25 °C, $VOCl_3$ external standard): δ −111.39 (t, J_{VP} = 420.58 Hz).

Generation of Cp(t-BuN)V(SPh)$_2$. To a reddish-brown solution of Cp(t-BuN)V(i-Pr_2N)Me (0.126 g, 0.420 mmol) in hexane (1 mL) was added a 1 mL hexane solution of PhSSPh (0.091 g, 0.42 mmol). After 5 h at 50 °C the mixture turned dark green. The solvent was subsequently pumped off, leaving the title compound as a green oil. ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 7.93 (d, J_{HH} = 7.7 Hz, 4H, SPh), 7.12 (d, J_{HH} = 7.6 Hz, 4H, SPh), 6.98−6.80 (m, 2H, SPh), 5.61 (s, 5H, Cp), 1.02 (s, 9H, t-BuN Me). ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 25 °C): δ 148.81 (SPh C_{ipso}), 132.81 (SPh CH), 128.28 (SPh CH), 125.94 (SPh CH), 108.17 (Cp), 30.07 (t-BuN Me), Cq of t-BuN not observed.

Catalytic Cyclotrimerization of Phenylacetylene Using Cp(RN)V(N-i-Pr_2)Me (R = p-Tol, t-Bu). All cyclotrimerization experiments were performed in NMR tubes equipped with a Teflon (Young) valve. To a solution of the precatalysts Cp(p-TolN)V(N-i-Pr_2)Me or Cp(t-BuN)V(N-i-Pr_2)Me (0.045 mmol) in benzene-d_6 (0.6 mL) was added 1 equiv of cyclohexane (0.045 mmol, 5 μL added via microsyringe), followed by 10 equiv of PhCCH (0.046 g, 0.45 mmol). The tube was placed at 80 °C and monitored by ^{1}H NMR spectroscopy. After completion of the reactions, the mixtures were analyzed by GC-MS and GC as well, using cyclohexane as internal standard (R_f = 1.02).

Catalytic Cyclotrimerization of Diphenylacetylene Using Cp(t-BuN)V(N-i-Pr_2)Me. The cyclotrimerization experiment was performed in an NMR tube equipped with a Teflon (Young) valve. A solution of Cp(t-BuN)V(N-i-Pr$_2$)Me (0.03 mmol, 0.010 g) in benzene-d_6 (0.6 mL) was made, and diphenylacetylene (0.30 mmol, 0.053 g) was added. The tube was warmed at 80 °C. After 3 h at this temperature white crystals started to form in the tube, and after 24 h the amount of crystals had increased considerably. The tube was kept at this temperature for another 60 h, after which the solid part was separated from the liquid by centrifuge. After washing with pentane (2 × 1 mL), white crystals of hexamethylbenzene were obtained in 71% yield. The product was identified by GC-MS analysis (THF solvent).

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Supporting Information Available: Crystallographic information files of compounds **2a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.